An overview of the role of goethite surfaces in the environment

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Abstract:

Goethite, one of the most thermodynamically stable iron oxides, has been extensively researched especially the structure (including surface structure), the adsorption capacity to anions, organic/organic acid (especially for the soil organic carbon) and cations in the natural environment and its potential application in environmental protection. For example, the adsorption of heavy metals by goethite can decrease the concentration of heavy metals in aqueous solution and immobilize; the adsorption to soil organic carbon can decrease the release of carbon and fix carbon. In this present overview, the possible physicochemical properties of the goethite surface contributing to the strong affinity of goethite to nutrients and contaminants in natural environment are reported. Moreover, these chemicals adsorbed by goethite were also summarized and the suggested adsorption mechanism for these adsorbates was elucidated, which will help us understand the role of goethite in natural environment and provide some information about goethite as an absorbent. In addition, the feasibility of goethite used as catalyst carrier and the precursor of NZVI was proposed for removal of environmental pollution.

Keywords: goethite, adsorption, catalysis, environmental remediation

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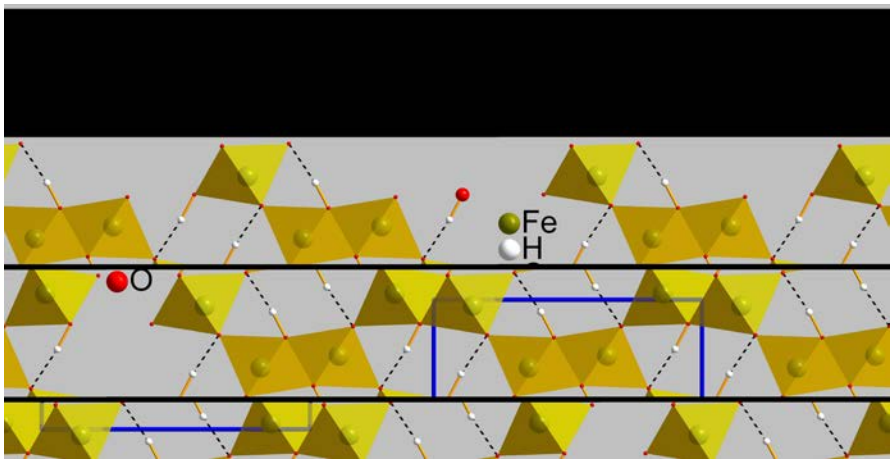
1. Introduction

Goethite (α-FeOOH) is a widespread soil mineral and a major component of many ores, sediments and soils and it is one of the most thermodynamically stable iron oxide (Cornell and Schwertmann, 2003). Goethite can be found in both humid and semiarid regions and also appears as the weathering product of various iron-containing rocks (Kemp, 1985). The orthorhombic structure of goethite has been confirmed as hexagonally close-packed array of O^{2-} and OH^{-} anions with Fe^{3+} in the center of the octahedral (Cornell and Schwertmann, 2003). The two octahedrons compose double chains of octahedra formed by edge sharing, running parallel to the [001] direction. Fig. 1 shows these chains are linked to adjacent double chains by corner-sharing with one chain and the OH groups are linked to another O atom in a chain diagonally opposite.



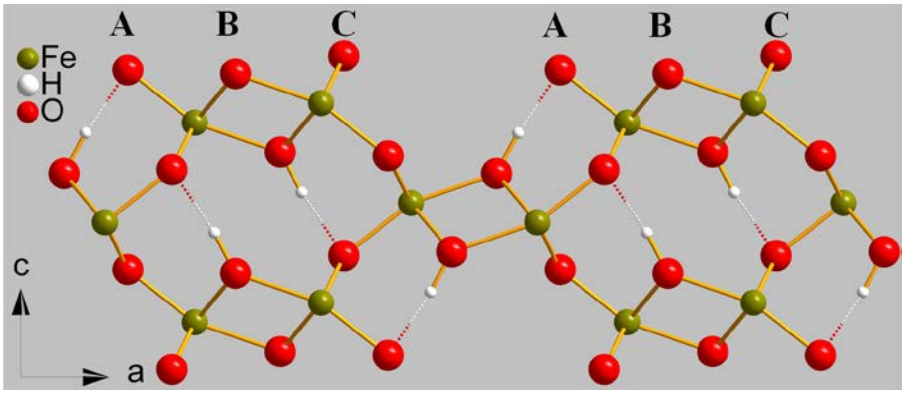


Fig. 1. (010) plane of goethite (top) polyhedral framework and (bottom) ball and stick model (Blue line represents unit cell and the dash line denotes the hydrogen bonding).

Generally, goethite can be found in pedosphere, hydrosphere and biosphere, resulting from rock weathering. In terms of goethite, it can derive from olivine or pyrite due to complicated processes including physical, chemical and biological. As is written in the book (Schwertmann and Cornell, 2000), the general formation process can be described as followed.

$$2Fe_2SiO_4 + O_2 + 6H_2O = 4\alpha\text{-}FeOOH + 2H_4SiO_4$$

$$4FeS_2 + 15O_2 + 10H_2O = 4\alpha\text{-}FeOOH + 8H_2SO_4$$

The newly formed goethite has a low solubility and it is the most stable iron oxyhydroxide in nature. Generally, goethite formed from weathering is often poorly crystalline and rich in defects and impurities, which makes goethite has much good surface activity. Moreover, goethite displays nanometer sized particles in width and several microns in length for both naturally formed and the laboratory synthesized analog. Such sizes make goethite with a high specific surface area, varying from 10-132 $m^2 \cdot g^{-1}$ (Atkinson et al., 1967; Strauss et al., 1997) depending on the transforming environment and the synthetic conditions. Therefore, the wide spread in nature and special physicochemical properties attracted many attentions on the study of the structure, surface physiochemical properties and adsorption capacity of goethite. As for the structure of goethite, the existence of bulk groups have been investigated widely using various techniques such as IR and TG/DTG (Russell et al., 1974; Schwertmann, 1984). In addition to this bulk groups, goethite still has a complicated surface structure especially the distribution of adsorbed water/hydroxyl group. In recent years, several reports about the fine surface structure can be found using crystal truncation rod (CTR) or model means. Ghose et al. reported that the proposed interface stoichiometry is (H_2O)-(H_2O)-OH_2-OH-Fe-O-O-Fe-R, which indicates the existence of two layers of absorbed water and two types of terminal hydroxyls, a hydroxo group and a aquo group (Ghose et al., 2010). The report of Boily (Boily, 2012) confirmed that interfacial water molecules adopted highly surface-specific configurations on (010), (100), (110), and (021) planes of goethite. Besides, water molecules generally had weaker hydrogen bonding strengths, as well as smaller self-diffusion coefficients, than their bulk liquid counterparts. Relevant reports on the surface functional groups (Fe-O, Fe-OH, Fe-O-Fe) calculated using density functional theory (DFT) or other

models can be found in the literature (Boily et al., 2001; Villalobos et al., 2003; Rustad and Boily, 2010). All these physicochemical properties imply goethite has a great potential as an adsorbent or catalyst due to its large surface area and special surface active sites.

The widespread occurrence and special physicochemical properties determine the significant role of goethite in nature and in the man-made environment. In the past several decades, goethite has been documented playing a crucial role in regulating the mobility and transformation of species in various parts of the ecosystem and their transport between these parts. It involves the uptake of plant nutrients from soil, the transportation of pesticides and other contaminants from soil to the aquatic system, and the purification of carbon-, sulfur- and nitrogen-containing gases (Russell et al., 1975; Kaneko and Inouye, 1981; Ishiwaka and Inouye, 1983; Baltrusaitis et al., 2007; Simonetti et al., 2007). In addition, goethite has been demonstrated to be a natural catalyst for catalytic oxidation of organic compounds in soil or wastewater (Lin and Gurol, 1996; Lu, 2000).

Under this research background, we have summarized the structure and promising values of goethite in the environment, as adsorbent for nutrients and as an adsorbent or/and catalyst for contaminants especially for organic substances and cations. As an important constituent of soil and sediments, it is essential to have a comprehensive understanding for its structure, especially for the surface functional groups, the physicochemical properties and its potential applications. As an abundant and cheap natural material with a large specific surface area and high surface reactivity, it is important and worthwhile to understand its potential applications in environmental protection. Nowadays, environmental pollutions are displaying a development of multi-dimension namely from ground surface to subsurface and air with the rapid economic development. Therefore, this present work reviews the research of goethite as an adsorbent or/and catalyst and reveals the implied significance to the environment. Meanwhile, the further possible applications as a precursor of multi-porous iron oxides or nZVI, which can be used in environment protection, are also suggested.

2. Surface properties of goethite

As is well known, goethite is isostructural with diaspore (α-AlOOH). However, it is the surface structure not the bulk structure that makes this kind of iron oxyhydroxide sensitive to the environment. From 1930s to now, several significant reports on the study of the structure

of goethite can be found using a range of different methods (Goldsztaub, 1932; Sampson, 1969; Gast et al., 1974; Busca et al., 1978; Rochester and Topham, 1979b; Schwertmann, 1984; Boily et al., 2001; Villalobos et al., 2003; Ghose et al., 2010; Rustad and Boily, 2010; Han et al., 2011; Boily, 2012) . Goldsztaub solved the crystal structure of goethite in 1932 and then Sampson reported the lattice parameters of a natural single crystal and synthetic goethite in 1969 (Goldsztaub, 1932; Sampson, 1969). Russell et al. investigated the types of goethite surface hydroxyl groups by characterizing goethite and phosphated goethite (Russell et al., 1974), which proves goethite has three types of surface hydroxyl groups as is shown in Fig. 1. More details about the surface hydroxyl groups were presented in the literature (Rochester and Topham, 1979b). DFT has been used for calculations of the vibrational frequencies of OH groups of an idealized goethite (110) surface (Rustad and Boily, 2010). Later, surface adsorbed water even the number of its layers was investigated. Robert et al. studied the interaction of water with goethite compared with other amorphous ferric oxides (Gast et al., 1974) . The results indicated that the last traces of physically adsorbed water were removed from the amorphous ferric oxides by outgassing at 25 ^{o}C, however, still retained approximately a monolayer of physically adsorbed water on goethite under the same conditions. This monolayer of water on goethite was proposed presumably hydrogen-bonded at least in part with the structural hydroxyls. Ghose et al. reported that the proposed interface stoichiometry is (H_2O)-(H_2O)-OH_2-OH-Fe-O-O-Fe-R, which indicated the existence of two layers of absorbed water and two types of terminal hydroxyls, a hydroxy group and an aquo group (Ghose et al., 2010). The bulk groups and the complicated surface functional groups results in the potential of strong affinity and high reactivity. The surface hydroxyl groups of goethite can promote more ·OH generation in the presence of ozone than that of β-FeOOH, γ-FeOOH and γ-AlOOH (Zhang et al., 2008). Furthermore, Liu et al. (Liu et al., 2013) postulated that not only the specific surface areas, but also the numbers of hydroxyl groups (namely effective adsorption sites) on goethite influences the adsorption capacity of goethite to phosphate.

3. Adsorbent

As an adsorbent, surface site density is an important factor determining the adsorption capacity of material. Villalobos et al. (Villalobos et al., 2003) investigated the surface site density of goethite by adsorption of proton and carbonate, indicating an inverse relationship between sorption capacity for protons and carbonate ions and specific surface area of goethite

for three synthetic goethite preparations. An explanation for this is the variability of the surface site density. Extra speculation was presumed depending on the different preparation methods which lead to different predominant faces for goethite. In addition, goethite usually presents large specific surface area as is mentioned above. All the confirmed information on the properties of goethite displays it possesses underlying predomination on physical, chemical and even biological reaction.

3.1 For anions

Table 1 lists the researched anions and relevant references in part, although it is confirmed there are more than 100 papers can be found on the research of inorganic anion adsorption on goethite. It mainly involves the effect of goethite on their transport, transformation and bioavailability. Furthermore, the effect of pH, ionic strength, exotic ions and temperature were also investigated. In these researches, some of the reported research mentioned the application of goethite for the treatment of environmental pollutants. The extent of goethite adsorption and the in-depth study of adsorption mechanisms substantially improved the understanding of the role of goethite in the environment.

According to the reported results and adsorption theory, the main adsorption mechanisms contain both non-specific adsorption and specific adsorption (ligand exchange). Hingston et al. illuminated both adsorption mechanisms in detail (Hingston et al., 1972). In aqueous suspension, the terminal iron atoms on the surface will complete their coordination shells with OH^- and water molecular. When the ions in solution do not have specific affinity for the iron atoms of the surface, the surface will adsorb H^+ and OH^-. In contrast, specific adsorption means replacement of hydroxyl groups by the adsorbing ligand. Specific adsorption frequently occurs for anions, in which phosphate and arsenate were most widely researched. At the earliest, Atkinson et al. proposed that phosphate replaces type A hydroxyl group and forms bridges between adjacent Fe^{3+} (Atkinson et al., 1972). Afterward, many reports can be found on the adsorption model of phosphate on the surface of goethite using various methods (Tejedor-Tejedor and Anderson, 1990; Torrent et al., 1990; Torrent et al., 1992; Geelhoed et al., 1997b; Strauss et al., 1997; Nowack and Stone, 1999a; Li and Stanforth, 2000; Ler and Stanforth, 2003; Lin et al., 2004; Chitrakar et al., 2006). Adsorption of phosphate on goethite mainly involves a ligand exchange mechanism which is similar to the adsorption of arsenate. Tejedor-Tejedor et al. studied the mechanism of phosphate adsorption on goethite using in-situ CIR-FTIR, which provided evidence for the formation of

three different type of complexes, protonated and nonprotonated bridging bidentate as well as a nonprotonated monodentate, between orthophosphate ions and surface Fe^{3+} of α-FeOOH particles in aqueous suspensions (Tejedor-Tejedor and Anderson, 1990). Hiemstra et al modeled phosphate adsorption on goethite with the CD-MUSIC using comparable experimental data, concluding the existence of monodentate species at very low surface loading. In fact, many researchers presented different ligand models considerably dependent on the surface coverage and solution pH. Generally, the bidentate surface complex is the most abundant for the adsorption of phosphate on goethite. Recently, the other mechanism of surface precipitation was reported by Josasson et al. (Jonasson et al., 1988), Li et al. (Li and Stanforth, 2000), and Ler et al. (Ler and Stanforth, 2003). Li et al. (Li and Stanforth, 2000) also investigated the distinction between the adsorption and surface precipitation of phosphate on goethite, which supposing the onset of surface precipitation occurs well before monolayer coverage, particularly at high pH values. Later, Ler et al. (Ler and Stanforth, 2003) confirmed the existence of surface precipitation of phosphate on goethite by monitoring the variation of ζ-potential of the phosphated goethite. The adsorption capacity of goethite to phosphate reached 10 mg-P/g-goethite (Chitrakar et al., 2006). In general, it is slow for the diffusion of phosphate adsorption between domains and for desorption of phosphate from goethite (Torrent et al., 1990; Strauss et al., 1997). The slow and even irreversible desorption for phosphate are attributed to slow rediffusion out of micropores, to the formation of inert, binuclear surface complexes, and to the affinity making goethite crystals into aggregates (Atkinson et al., 1972; Anderson et al., 1985).

The adsorption of chromate and arsenate/arsenite is also widely investigated due to their toxicity to humans (Abdel-Samad and Watson, 1997; Fendorf et al., 1997; Manning et al., 1998; Gao and Mucci, 2001; Rietra et al., 2001a; Gräfe et al., 2004; Lakshmipathiraj et al., 2006; Luengo et al., 2007; Zhang et al., 2007; Grafe et al., 2008; Amstaetter et al., 2009; Dimirkou et al., 2009; Catalano et al., 2011; Das et al., 2011; Guo et al., 2013a; Wang et al., 2013). The chromium XPS signal indicated that initially a small amount of chromium adsorbs in the Cr^{3+} oxidation state via a redox reaction, but that the large majority of chromium remains in the Cr^{6+} oxidation state (Abdel-Samad and Watson, 1997). As for the adsorption model, Fendorf et al. (Fendorf et al., 1997) gave a detailed account that chromate or arsenate retention on goethite is due to a monodentate complex at very low coverage, both the monodentate and bidentate complexes at intermediate coverage, and predominantly the

206 bidentate complexes at very high coverage. It indicates that the adsorption model for both
207 chromate and arsenate is strongly dependent on the surface coverage. In case of the effect of
208 pH, it is different for arsenate and arsenite. Arsenite adsorption increases with increasing pH,
209 as compared to low pH which improves the adsorption of arsenate. Lakshmipathiraj et al.
210 (Lakshmipathiraj et al., 2006) reported the adsorption amount of goethite to arsenate
211 decreased from 4.7 to 1.1 $mg \cdot g^{-1}$ as the pH increased from 5 to 8. Additionally, competitive
212 adsorption on goethite also has been the subject of much research because the competitive
213 adsorption results at least to some extent, affects the bioavailability of nutrients and
214 immobilization of toxic chemicals, such as the competitive adsorption between phosphate and
215 sulfate/arsenate (Geelhoed et al., 1997b; Gao and Mucci, 2003).

216

217 The adsorption of goethite for other anions was also studied including silicate, chloride,
218 fluoride and sulphate, and others, which reveals the universality of goethite adsorption. The
219 adsorption capacity and strong affinity of goethite to these adsorbates confirmed the
220 significance of goethite at least on their transport in environments.

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222

223 **Table 1. List for inorganic anion adsorption on goethite**

Inorganic anions	References
Silicate	(Hingston et al., 1967)
Selenite /Selenate	(Hingston et al., 1968; Manceau and Charlet, 1994; Saeki and Matsumoto, 1998; Rietra et al., 2001a; Das et al., 2013)
Phosphate	(Atkinson et al., 1972; Parfitt et al., 1975; Sigg and Stumm, 1981; Geelhoed et al., 1997a; Geelhoed et al., 1997b; Strauss et al., 1997; Venema et al., 1997; Geelhoed et al., 1998; Barrow, 1999; Nowack and Stone, 1999b; Li and Stanforth, 2000; Gao and Mucci, 2001; Dideriksen and Stipp, 2003; Gao and Mucci, 2003; Ler and Stanforth, 2003; Gimsing et al., 2004; Lin et al., 2004; Wang and Xing, 2004; Antelo et al., 2005; Chitrakar et al.,

	2006; Nowack and Stone, 2006; Cheng et al., 2007; Luengo et al., 2007; Rahnemaie et al., 2007; Kim et al., 2011)
Fluoride	(Hingston et al., 1972; Sigg and Stumm, 1981; Hiemstra and Van Riemsdijk, 2000)
Chloride	(Hingston et al., 1972)
Sulphate	(Hingston et al., 1972; Sigg and Stumm, 1981; Geelhoed et al., 1997a; Geelhoed et al., 1997b; Peak et al., 1999; Rietra et al., 1999; Rietra et al., 2001a; Juang and Wu, 2002; Beattie et al., 2008)
Silicate	(Sigg and Stumm, 1981; Kersten and Vlasova, 2009)
Arsenate/Arsenite/Arsenic	(Grossl and Sparks, 1995; Fendorf et al., 1997; Matis et al., 1997; Manning et al., 1998; Gao and Mucci, 2001; Liu et al., 2001; Waltham and Eick, 2002; Gao and Mucci, 2003; Gräfe et al., 2004; Antelo et al., 2005; Gräfe and Sparks, 2005; Dixit and Hering, 2006; Lakshmipathiraj et al., 2006; Giménez et al., 2007; Luengo et al., 2007; Sahai et al., 2007; Stachowicz et al., 2007; Grafe et al., 2008; Luxton et al., 2008; Stachowicz et al., 2008; Asta et al., 2009; Dimirkou et al., 2009; Hartzog et al., 2009; Catalano et al., 2011; Mamindy-Pajany et al., 2011; Wang et al., 2013)
Chromate	(Abdel-Samad and Watson, 1997; Fendorf et al., 1997)
Carbonate	(Hiemstra et al., 2004; Rahnemaie et al., 2007)

3.2 For organic compounds and organic acids

Table 2 displays the list of goethite adsorption of organic compound and organic acid. The adsorption/desorption behavior of water-soluble organics on goethite has been researched for several decades due to its significance on the transport and transformation of

organic compounds in soil and groundwater as well as the use of surfactants in the flotation of minerals (Tejedor-Tejedor et al., 1992). Therefore, this overview summarizes the adsorption behavior of fulvic acid, humic acid and glycophosphate, etc. on goethite. Generally, adsorption of organic on goethite is usually dominated by electrostatic effects, although ligand exchange and hydrogen bonding may also be involved (Cornell and Schwertmann, 2003).

Totally, organic compound adsorption on goethite usually depends on the solution pH, chemical composition of organic matter, ionic strength, composition of cation in solution. As for pH, solution pH<PZC will benefit the increase of adsorption capacity, and vice versa. Example is the decrease of the adsorption of lactate, tartrate and citrate with increasing pH (Cornell and Schindler, 1980). Moreover, low pH favors the inner-sphere surface complex at least for oxalate and malonate (Persson and Axe, 2005). Fu et al. (Fu and Quan, 2006) found the inner-sphere surface complex of fulvic on goethite which is consistent with the previously reported (Filius et al., 2000) which revealed a inner-sphere in low pH in contrast a out-sphere in high pH. In contrast, acetate, benzoate, and cyclohexanecarboxylate got a out-sphere surface complex as can be seen in the report (Norén and Persson, 2007). To the best of our knowledge, the adsorption model for organic also has a little difference, which has been widely researched using diffuse reflectance infrared Fourier transform, attenuated total reflectance Fourier transform infrared, X-ray photoelectron spectroscopy, atomic force microscopy, Extended X-Ray Adsorption Fine Structure, etc. Barja et al. (Barja and dos Santos Afonso, 2004) reported two predominating complexes where the phosphonate group in glyphosate or aminomethylphosphonic acid (a product of biodegradation of glyphosate) bonds monodentately or bridges bidentately to the surface of iron oxide in an inner sphere mode, while the carboxylate and amino group are noncoordinated to the surface. As for the adsorption model, different authors had different results for the same organic. Using citrate as an example, Cornell et al. (Cornell and Schindler, 1980) supported a tridenate complex according to the results of IR; however, Filius et al. (Filius et al., 1997) supported a bidentate complex based on their modeling work. Besides, organic acids, such as humic acid, still can improve the adsorption capacity of goethite for other organic compounds. Lglesias and coauthors (Iglesias et al., 2010) found the adsorption amount of paraquat dramatically increased from 0.03 to 0.24 $\mu mol \cdot (m^2)^{-1}$ as goethite was replaced by humic-coated goethite which was confirmed by Briganate et al. (Brigante et al., 2010) and later proposed the

adsorption mechanism. The same authors made another similar conclusion that humic-coated goethite favored the adsorption of MCPA ((4-chloro-2-methylphenoxy)-acetic acid, a kind of acid pesticide) at all concentrations of this pesticide. In addition, fulvic acid increased the adsorption of cadmium on goethite at low pH(<7) and decreased that at high pH(>7), and improved the adsorption of mercury within the whole pH interval (Bäckström et al., 2003). This adsorption, especially for natural organic matter (NOM), has another important significance in affecting the global carbon balance by protecting NOM from enzymatic oxidation to CO_2 in soil and sediments. Goethite not only influences the transport of these organic/organic acid listed in the table below, but also passively affects their transformation by surface complexation.

275 **Table 2. List for organic compound and organic acid adsorption on goethite**

Organic/organic acid	References
Acetate	(Sigg and Stumm, 1981; Norén and Persson, 2007)
Benzoic/benzoate	(Tejedor-Tejedor et al., 1992; Norén and Persson, 2007)
Phenolic	(Tejedor-Tejedor et al., 1992)
Citrate	(Geelhoed et al., 1998; Barrow, 1999; Lindegren et al., 2009)
Methylphosphonic Acid	(Barja et al., 1999)
Malonate	(Filius et al., 1999; Persson and Axe, 2005; Axe et al., 2006)
Phosphonate	(Nowack and Stone, 1999a; Mustafa et al., 2006)
Benzenecarboxylate/benzencarboxylic	(Boily et al., 2000; Lindegren and Persson, 2010)
Fulvic acid	(Filius et al., 2000; Weng et al., 2005; Fu and Quan, 2006; Weng et al., 2006b)
Humic acid	(Saito et al., 2003; Weng et al., 2006a; Kang and Xing, 2008)
Anthracene	(Angove et al., 2002)
Glyphosate	(Dideriksen and Stipp, 2003; Sheals et al., 2003; Barja and dos Santos Afonso, 2004; Gimsing et al., 2004; Jonsson et al., 2008)
Aminomethylphosphonic Acid	(Barja and dos Santos Afonso, 2004)
Oxalate	(Persson and Axe, 2005; Axe et al., 2006)
Mellitic acid	(Angove et al., 2006)
Bisphenol A (BPA)	(Shareef et al., 2006)
17α-ethynylestradiol (EE2)	(Shareef et al., 2006)
Estrone (E1)	(Shareef et al., 2006)
Molybdate	(Xu et al., 2006a, b)
Tetrathiomolybdate	(Xu et al., 2006a)

1-hydroxy-2-naphthoic acid	(Hanna and Carteret, 2007)
Silicic acid	(Hiemstra et al., 2007)
Fipronil	(Miranda Masutti and Mermut, 2007)
Ciprofloxacin	(Trivedi and Vasudevan, 2007; Carrasquillo et al., 2008)
p-Arsanilic Acid	(Depalma et al., 2008)
Polycyclic aromatic hydrocarbon	(Tunega et al., 2009)
Paraquat	(Brigante et al., 2010)
2-Ketogluconate	(Journey et al., 2010)
Glucose	(Olsson et al., 2011)
Methylene Blue	(Nassar and Ringsred, 2012)
Catechol	(Yang et al., 2012)
Tylosin	(Guo et al., 2013b)
Sulfamethazine	(Guo et al., 2013b)

3.3 For cations

Table lists the cations adsorption on goethite. On the whole, the possibility of adsorption on goethite to these mentioned metal ions have been documented and the strength of some of them on goethite decreases in the order: Cu>Pb>Zn>Cd>Co>Ni>Mn (Grimme, 1968; Gerth and Brümmer, 1983). Cation adsorption may be suppressed as the ionic strength increases and generally this is considered as an out-sphere adsorption (R-O-M, M presents the cations, R denotes the bulk), although it may be also the result of ion pairing in solution. Moreover, the affinity of cations for goethite is strongly dependent on the temperature of the system and on the time allowed for adsorption (Bruemmer et al., 1988). It was proposed that the process involved rapid adsorption on the external surface surfaces of crystals followed by slow diffusion into the internal sites, possibly along the domain boundaries, with finally, adsorption on internal sites (Cornell and Schwertmann, 2003). Hu et al. (Hu et al., 2010) investigated the effect of adsorption temperature, pH and ionic strength on the adsorption of radionickel on goethite. The results showed that the adsorption of Ni^{2+} was strongly dependent on the pH, ionic strength and temperature, indicating high temperature and high pH, low ionic strength favored the increase of Ni^{2+} adsorption. Still, the adsorption of Ni^{2+} was dominated by out-sphere surface complex at low pH in contrast to the inner-sphere at

high pH. Desorption is unavoidable after desorption, which depends on the types of metal and surface complexes formed. For example, Pb^{2+} can desorb completely from goethite whereas Cu, Zn, Cd, Ni and Co displayed hysteresis and Al as well as Np showed a extremely slow desorption (Padmanabham, 1983a, b; Lövgren et al., 1990; Tinnacher et al., 2011). The slow desorption should be ascribed to the inner-sphere surface complex and high affinity between metal and goethite. Besides, ternary adsorption, usually formed in the presence of anions and organic acids, also devotes a lot for the slow desorption of adsorbed metal ions. Fulvic acid can improve the adsorption of mercury and cadmium, citric acid and tartaric acid (at low concentration<1.0 mM) increased the adsorption of Cd^{2+} onto goethite (Huang et al., 2010). Fulvic acid and phosphate enhanced the adsorption of Th^{4+} was also confirmed (Yan et al., 2011). Perelomov et al. revealed the final Cu^{2+} adsorbed/Pb^{2+} adsorbed molar ratio was 1.58 in the absence of oxalic acid but greater than 2 in the presence of the organic ligand. Furthermore, most of previous investigations have suggested that humic substance promoted the adsorption of metal ions at low pH, such as the report of Ali et al. (Ali and Dzombak, 1996). The increase of adsorption was attributed to the adsorption of anions/organic acid on the mineral surface followed by the interaction of heavy metal ions with modified surface and generally formed ternary adsorption. Therefore, goethite is playing an important role in the water/particles system on the adsorption/desorption of metal ions, which is also affected in the presence/absence of natural organic matter, such as humic acid and fulvic acid.

Table 3. List for cation adsorption on goethite

Cation	References
Cd^{2+}	(Forbes et al., 1976; Angove et al., 1999; Buerge-Weirich et al., 2002; Wang and Xing, 2002; Bäckström et al., 2003; Buerge-Weirich et al., 2003; Mustafa et al., 2004; Wang and Xing, 2004; Mustafa et al., 2006; Dimirkou et al., 2009; Swedlund et al., 2009)
Co^{2+}	(Forbes et al., 1976; Angove et al., 1999)
Cu^{2+}	(Forbes et al., 1976; Grossl and Sparks, 1995; Kooner et al., 1995; Ali and Dzombak, 1996; Rodda et al., 1996; Robertson and Leckie, 1998; Buerge-Weirich et al., 2002; Juang and Wu, 2002; Buerge-Weirich et al., 2003; Sheals et al., 2003; Lin et al., 2004; Huerta-Diaz, 2006; Jonsson et al., 2006; Grafe et al.,

	2008; Weng et al., 2008; Swedlund et al., 2009; Perelomov et al., 2011)
Pb^{2+}	(Forbes et al., 1976; Kooner et al., 1995; Abdel-Samad and Watson, 1998; Kraemer et al., 1999; Kovačević et al., 2000; Ostergren et al., 2000a; Ostergren et al., 2000b; Villalobos et al., 2001; Glover et al., 2002; Wu et al., 2003; Orsetti et al., 2006; Garman et al., 2007; Swedlund et al., 2009; Perelomov et al., 2011)
Zn^{2+}	(Forbes et al., 1976; Kooner et al., 1995; Kosmulski et al., 2003; Gräfe and Sparks, 2005; Xu et al., 2006c; Wang et al., 2008; Perelomov et al., 2011)
Ca^{2+}	(Ali and Dzombak, 1996; Rietra et al., 2001b; Kosmulski et al., 2003; Weng et al., 2005; Weng et al., 2008)
Cd^{2+}	(Davis and Upadhyaya, 1996; Venema et al., 1996; Collins et al., 1999a; Glover et al., 2002; Granados-Correa et al., 2011)
Cr^{6+}	(Villalobos et al., 2001)
Ni^{2+}	(Buerge-Weirich et al., 2002; Buerge-Weirich et al., 2003; Xu et al., 2006c; Marcussen et al., 2009)
Hg^{2+}	(Collins et al., 1999b; Bäckström et al., 2003)
Sr^{2+}	(Sahai et al., 2000)
U^{6+}	(Giammar and Hering, 2001; Villalobos et al., 2001; Missana et al., 2003; Cheng et al., 2004; Cheng et al., 2007; Sherman et al., 2008; Guo et al., 2009; Yusan and Erenturk, 2011; Singh et al., 2012)
V^{5+}	(Peacock and Sherman, 2004)
Sb^{3+}/Sb^{5+}	(Leuz et al., 2006; Watkins et al., 2006; Martínez‐Lladó et al., 2008)
Ga^{3+}	(Persson et al., 2006)
Ge^{4+}	(Pokrovsky et al., 2006)
Se^{4+}/Se^{6+}	(Rovira et al., 2008)
Np^{5+}	(Tinnacher et al., 2011)
Th^{4+}	(Yan et al., 2011)
Nd^{3+}	(Armstrong and Wood, 2012)

3.4 For gases

Goethite was seldom used as a gas adsorbent. On the other hand, various gases were often utilized as probe molecules and provide information about the surface properties, such as surface acid-base nature and surface adsorption sites. Russell et al. (Russell et al., 1975) reported the CO_2 is strongly adsorbed as CO_3^{2-} on moist goethite surface, but as both CO_3^{2-} and HCO_3^- on dry surfaces. The adsorbed carbonate played a role in redistributing surface charge and similar role was proposed to extent to other anions such as phosphate. Afterward, infrared spectra were recorded of pyridine, acetic acid, nitric acid and trimethylchlorosilane adsorbed on the surface of goethite, which confirmed the relationship between the adsorption characteristic and the surface Lewis acid sites of goethite (Rochester and Topham, 1979a). Furthermore, NO was demonstrated to be adsorbed more strongly than SO_2 and CO_2 and NO can displace previously adsorbed SO_2 and CO_2 from the surface of goethite (Ishiwaka and Inouye, 1983). The adsorption of SO_2 and NO on the surface of the goethite increased the electrical conductivity which accelerated atmospheric corrosion of steel (Kaneko and Inouye, 1981; Kaneko and Matsumoto, 1989; Baltrusaitis et al., 2007). The bright side is the potential application as a catalyst or catalyst carrier for selective catalytic reduction (SCR) to be determined in future, which is being investigated by our research group. Recently, Simonetti et al. investigated the electronic structure of S and H_2S adsorbed on the goethite (110) surface by AESD-MO cluster calculations (Simonetti et al., 2006; Simonetti et al., 2007). The results showed that $S\text{-}H_{(goethite)}$ is the major interaction for S and H_2S, indicating hydrogen bonding contributed the interaction between S and H_2S and goethite. Although goethite has not been researched as adsorbent or catalyst for sulfide at present, it is presumed this will attract much attention on desulfurization and denitrification in industries due to goethite affinity to N-containing and S-containing gases. The significance of goethite in the environment still embodies the immobilization of dissolved goethite to generated CO_2. Yao et al. (Yao et al., 2013) investigated the effect of goethite on the release of methane in the anaerobic biochemical system consisted of dissimilar iron-reducing bacteria and methane-producing bacteria. The results indicated that the maximum cumulative production of methane was brought forward by 60 to 78 d in the presence of goethite and CO_2 was decreased by 30 to 67% compared with that without goethite.

4. Catalysts

Except for the adsorption of anions, organics and organic acid, cations and gases, goethite still decomposes or catalytic decomposition of some contaminants in the absence and presence of hydrogen peroxide and/or UV radiation. Recently, Han et al. first reported that aqueous goethite can generate singlet oxygen and hydroxyl radical under room light and aeration conditions investigated using spin-trapping electron paramagnetic resonance and H_2O_2 can improve the generation of both reactive species (Han et al., 2011). Table 4 lists the references on the application of goethite as a catalyst. The main mechanism for catalytic reactions involved the generation of hydroxyl radicals both directly or indirectly. Like the adsorption of goethite to organics, the catalysis behavior is also strongly dependent on the solution pH. As a catalyst, goethite was seldom researched before the 21th century. Hydroquinone can be converted into quinine in the presence of finely divided goethite in slightly acid solutions (Shindo and Huang, 1984). Cunningham et al. (Cunningham et al., 1988) reported benzoate, oxalate, and succinate adsorbed goethite in slightly acid solution were degraded under in the presence of UV and revealed the reaction mechanism by detecting the products of Fe^{2+} and ·OH. In the recent decade, increasing attention was paid to this kind of natural phenomenon and potential environmental application related to goethite due to its special surface properties, such as large surface area and high surface hydroxyl content. Muruganandham et al. (Muruganandham and Wu, 2007) investigated the decomposition of dissolved ozone in the presence of granular goethite to reduce the residual ozone in treated water and the decomposition of ozone increased from 53.2 to 98% as the goethite loading increased from 2 to 30 $g \cdot L^{-1}$. The results indicated granular goethite is a promising catalyst for the decomposition of ozone in aqueous medium. Oxalate and salicylate have a competitive adsorption on goethite, however, the existence of oxalate improved the photodegradation of salicylate by reacting with goethite producing OH radicals (Krýsa et al., 2011). BPA also can be degraded by goethite suspensions and acidic solutions accelerated the reaction, which implies goethite may play a crucial role in the abiotic attenuation of BPA in the natural environment (Lin et al., 2012). A direct evidence for the significance of goethite in environment is the photooxidation of arsenite to lowly toxic arsenate in the natural goethite suspension. In addition, improved oxidation will substantially occur in the presence of hydrogen peroxide and/or UV radiation in the presence of goethite. Lu et al. (Lu, 2000) reported the 2-chlorophenol can be decomposed with hydrogen peroxide catalyzed by goethite and the oxidation rate increased with the decrease of goethite particle size. He et al. (He et al., 2005) found that aromatic compounds could undergo rapid decomposition and

mineralization (even to 100% yield) in the presence of both a-FeOOH and H_2O_2 under UV irradiation, and the degradation rates of the organics were related to their sorption ability of the surface of a-FeOOH and were in the following order: salicylic acid≈m-hydroxylbenzoic acid > p-hydroxylbenzoic acid ≈ benzoic acid > p-biphthalic acid > phenol > benzenesulfonic acid. The results imply the role of goethite in the transportation and photochemical processes of NOM in the natural environment. Not only UV, but also ultrasonic irradiation can enhance the catalytic activity of goethite-H_2O_2 system. The decoloration of dye was strongly enhanced by ultrasonic irradiation on Fenton-like process, namely goethite-H_2O_2 system, based on the research of Muruganandham et al. (Muruganandham et al., 2006). The similar result can be found in the report (Wu et al., 2012) indicating goethite surfaces catalysed a Fenton-like reaction responsible for the decolorizing of azo dye Orange G. Furthermore, goethite still can catalyze ozonation. Zhang et al. (Zhang and Ma, 2008) reported that catalytic ozonation with goethite can substantially enhance nitrobenzene decomposition compared with ozonation alone. It is speculated this phenomenon is closely related to the decomposition of dissolved ozone in goethite suspension as is mentioned above.

Table 4. List for the catalytic reaction

Reactant	References
N-butyl chloride	(Lin and Gurol, 1996)
2-chlorophenol	(Lu, 2000; Lu et al., 2002)
2,6-dimethylphenol	(Mazellier and Bolte, 2000)
3,4-dihydroxybenzoic acid	(Andreozzi et al., 2002a)
1,2-benzenediol (catechol)	(Andreozzi et al., 2002b)
2-aminophenol	(Andreozzi et al., 2002b)
2,3-dihydroxybenzoic acid	(Andreozzi et al., 2002b)
Disinfection Byproducts	(Chun et al., 2005)
Aromatic compounds	(He et al., 2005)
4-chloronitrobenzene	(Chun et al., 2006)
Trichloronitromethane	(Chun et al., 2006)
Direct Orange 39 (DO39) azo dye	(Muruganandham et al., 2006)
Polyethylene	(Liu et al., 2009)
C.I. Acid Orange 7	(Zhang et al., 2009)

Bisphenol A	(Lin et al., 2012)
Trimethyl Phosphate	(Mäkie et al., 2012)
Triethyl Phosphate	(Mäkie et al., 2012)
Azo dye Orange G	(Wu et al., 2012)
Oxalate	(Krýsa et al., 2011)

5. Effect of Al substitution

Goethite has a similar structure with diaspore and the 6-fold coordinated Fe has been demonstrated to be replaced usually by Al, Co, Mn, Cr, Ni, etc., among which the substitution of Al for Fe was well documented and was also demonstrated to occur in natural goethite (Norrish and Taylor, 1961; Mendelovici et al., 1979; Fitzpatrick and Schwertmann, 1982; Cornell and Schwertmann, 2003). In addition, Al-substituted goethite can also be synthesized easily in the laboratory. The Al substitution for Fe significantly affects the physicochemical properties, which has been studied by many researchers using different modern techniques, such as XRD, TG/DTG/DTA, TEM, IR, SEM, Mössbauer spectra, etc. (Golden et al., 1979; Mendelovici et al., 1979; Fey and Dixon, 1981; Goodman and Lewis, 1981; Fysh and Fredericks, 1983; Schulze, 1984; Schulze and Schwertmann, 1984; Schulze and Schwertmann, 1987; Schwertmann and Murad, 1990; Ruan and Gilkes, 1995; Scheinost et al., 1999; Ruan et al., 2002; Blanch et al., 2008; Morozov and Vasil'ev, 2010; Liu et al., 2012b; Liu et al., 2012c). Ainsworth et al. (Ainsworth and Sumner, 1985; Ainsworth et al., 1985) postulated that the occurrence of Al substitution for Fe in the structure of goethite may sterically hinder the sorption of phosphate on goethite, although the substitution increased the specific surface area and improved the isotopic exchange rates. However, in recent years, Al-substituted-goethite also exhibited higher specific surface area and higher adsorption capacity for Cu, Zn and Cd ions compared to pure goethite (Spathariotis and Kallianou, 2007). The results were similar with the current report indicating the presence of structural Al in the goethite enhanced considerably the As uptake capacity and also decreased the mobilization of Fe and As adsorbed as the substitution amount increased. However, whether the increased specific surface area or the substitution of Al for Fe improved the adsorption capacity is still not confirmed since the substitution of Al generally favors the increase of surface area.

6. Conclusions and summary

As is mentioned above, goethite has an isostructure with diaspore. However, it generally has a size in nanometers in width and several microns in length, which presumably results in the large specific surface area. Combining with the abundant surface hydroxyl groups, goethite is playing an important role in the transport and transformation of nutrients and contaminants containing anions, organic/organic acid (including soil organic carbon), cations and some gases. The adsorption of goethite to nutrients can decrease their loss; the adsorption to heavy metals can reduce their concentration in aqueous solution; the adsorption to soil organic carbon can reduce the release of carbon from soil, which at some degree can fix carbon. Although these gases were selected as probe molecule to characterize the surface properties of goethite, the results still displayed a selective adsorption of goethite to NO compared with SO_2 and CO_2. As for other nutrients and contaminants, goethite showed a good affinity by non-specific adsorption, specific adsorption (ligand exchange) and ternary adsorption. Non-specific adsorption, in general, occurs for the ions which have specific affinity for the metal atoms of the surface, e.g. $NaNO_3$, and then was absorbed by electrostatic interaction. Specific adsorption frequently happened for organic/organic acid by surface complexation (inner-sphere complexation), such as phosphate and citrate, while ternary adsorption generally takes place for the mixture of organic/organic acid and cations where cations were adsorbed by the linkage of organic/organic acid. Basically, all the adsorption is strongly dependent on the solution pH. In addition, goethite surfaces showed preferential adsorption of P-containing and high molar mass organic solutes, but not of N-containing compounds. The strength of surface affinity of goethite to metals generally decreases in the order: Cu>Pb>Zn>Cd>Co>Ni>Mn.

According to the overview, goethite has a crucial significance in the natural environment. Based on the property, recently, natural goethite and synthetic goethite were also researched as catalyst carrier and precursor of nano zero valent iron (NZVI) for treatment of aqueous contaminants in our group. Liu et al. (Liu et al., 2012a) investigated the effect of carrier (natural goethite, synthetic goethite and palygorskite) on catalytic cracking of biomass tar, which indicated that goethite as a carrier had the best catalytic reactivity. Afterward, natural goethite was selected to prepare NZVI to remove nitrite and nitrate and compared with the ordinary iron powder, which also presented the natural goethite as a precursor had a good reactivity in decomposition of nitrite and nitrate (Liu et al., 2012d). This year, NZVI prepared by reducing natural goethite in hydrogen was considered to remove phosphate and p-

nitrophenol (PNP). This kind of NZVI displayed good adsorption efficiency and reduction efficiency, respectively, and the former is in the process of under review and the latter is being completed. In addition, the role of goethite in accelerating the generation of methane and hindering the production of CO_2 in anaerobic decomposition of organics was confirmed. Therefore, goethite is really playing a crucial role in the transport and transformation of anions, organic/organic acid, cations and gases in environments. Furthermore, the significance of goethite is presumably to be expanded based on the inherent properties, such as large specific surface area and abundant hydroxyl groups in the bulk as well as on the surfaces. Goethite as the precursor of nano-hematite, nano-magnetite and NZVI is being or going to be considered in the future.

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Table captions

Table 1. List for inorganic anion adsorption on goethite

Table 2. List for organic compound and organic acid adsorption on goethite

Table 3. List for cation adsorption on goethite

Table 4. List for the catalytic reaction

Figure captions

Fig. 1. (010) plane of goethite (top) polyhedral framework and (bottom) ball and stick model